BIOPETROL SYNTHESIZED FROM RUBBER SEED'S FATTY ACID USING FULLER'S EARTH AS CATALYST

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A**BSTRACT**

Ever since it was known that fossil fuel are finite, scientists has been looking for alternative energy to replace fossil fuel. Biopetrol mostly derived from vegetable oils and hence it can be categories as a renewable fuel. However the usage of vegetable oil for biopetrol will put a pressure onto the food demands and its best to be ease by using new and unexploited oil crops capable of producing fats and oil for the industry where in this topic, rubber seed. The main objective is to synthesize biopetrol from fatty acids obtain from rubber seeds via catalytic cracking using fuller earth as catalyst. Long chain of fatty acid will be break down into smaller chain. The process is done by extracting oil from rubber seed via soxhlet extraction method using hexane as the extractor. The excess hexane is removed by using rotary evaporator and the extracted purified oil is then mixed together with fuller earth and continuously heated and stir for 2hours. Rubber seed oil that has been cracked with 20g fuller's earth is then diluted into 4 different mixtures with hexane as solvent-1%, 5%, 10%, 20%. About 1.5 ml of each sample is injected trough 0.2 through 0.2μm syringe filter into each vials which contains mixture samples before proceed to analyzing using gas chromatography. Isooctane obtained is around 64%-111% in Rubber seed extracted by using fuller earth. This is due to various factor such as random reaction in catalytic cracking, porosity property of fuller earth, unmodified gc peak area that cause the existence of impurities and contamination of the apparatus. Isoocatane can be successfully synthesis from rubber seed by using fuller earth as catalyst.

ABSTRAK

Sejak manusia mengetahui bahawa kuantiti bahan api adalah terhad, para penyelidik telah berusaha mencari jalan alternatif bagi menyelesaikan masalah ini. Biopetrol yang kebiasaannya diperoleh dari minyak sayuran menjadi pilihan membolehkan minyak ini dikategorikan sebagai sumber tenaga yang boleh diperbaharui. Namun, pengunaan minyak sayuran boleh menyebabkan peningkatan terhadap permintaan makanan maka adalah digalakan untuk mencari sumber alternatif lain yang mempunyai kebolehan untuk menghasilkan lemak dan minyak dan; salah satu contohnya adalah biji getah. Objektif utama adalah untuk menyentisis biopetrol dari asid lemak yang diperoleh dari biji getah melalui pemecahan pemangkin mengunakan Fuller's Earth sebagai pemangkin. Rantai panjang asid lemak akan dipecahkan menjadi pendek. Kerja ini dilakukan dengan mengekstrak minyak dari biji getah melalui sulingan soxhlet dengan hexane sebagai pengektrak. Lebihan hexane akan dibuang dengan mengunakan rotary extractor. Minyak yang diextract akan dicampur bersama-sama dengan 20g Fuller's Earth dan die panaskan selama 2jam. Minyak yang sudah melalui pemecahan pemangkin akan cairkan dengan hexane sebagai pelarut-1%,5%,10% dan 20%. Lebih kurang 1.5ml akan ditapis mengunakan 0.2-0.2 μm penapis syringe kedalam sebelum melakukan analisis mengunagakn gas chromatography. Jumlah isooctane yang diperolehi adalah antara 64% ke 111%. Ini mungkin disebabkan oleh tindak balas rawak semasa pemecahan pemangkin berlaku, keadaan fizikal Fuller's Earth, bacaan gas Chromatography yang menunjukan kehadiran bendasing dan juga kekotoran dalam alat radas. Isooctane yang merupakan komposisi penting dalam biopetrol dapat dicerakinkan dari minyak biji getah dengan mengunakan Fuller Earth sebagai pemangkin.

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LIST OF SYMBOLS

P	-	Pressure
m	-	Mass
ΔH	-	Enthalpy change of reaction
ΔS	-	Entropy change of reaction
ΔG	-	Energy change of reaction
T	-	Temperature
ρ	-	Density
μ	-	Viscosity of liquid (Pa.s)
h	-	Heat transfer coefficient
^{o}C	-	Degree Celsius
kg	-	Kilogram
K	-	Degree Kelvin
m	-	Meter
n	-	Number of moles
L	-	Liter

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Ever since it was known that fossil fuel are finite; scientists has been looking for an alternative energy to replace fossil fuel. Through various research, biodiesel has been proven as one of the best replacement for fossil fuel, diesel. This breakthrough has been set a marking stone to further research into other type of fuels such as biopetrol and bioethanol.

Biopetrol is derived from vegetable oils and hence it is a renewable fuel. Its desired characteristics which are no sulfur content, no storage difficulty, excellent lubrication properties, non toxic, renewable sources and is biodegradable has made it the best alternative for fossil fuel. However the usage of vegetable oil for biopetrol will put a pressure onto food demands; therefore it is best to be eased by developing a new and unexploited oil crops capable of producing fats and oil for the industry.

Approximately there are about one million rubber trees in Malaysia. A mature rubber tree can produce seeds but sadly; these seeds are left to waste instead of the usage or ability of the seeds being expanded.

Oleic acid is a monounsaturated of fatty acid that can be found in all vegetable oil including rubber seeds. Catalytic cracking method will be used to break hydrocarbon chain in the oleic acid to produce isooctane by using the fuller's earth as catalyst. Isooctane is known to have similar property as petrol.

1.2 Problem statement

Petroleum is a non renewable energy source. It takes thousands of years to form naturally and cannot be replaced as fast as they are being consumed. The increasing demands and the limited resources have caused the oil price to increase dramatically. Even though the oil price today is much lower than the oil price of the year 2006, the unstable spike of the oil price can move as far as they like, and we are prone to face another oil spike which will eventually topple the highest price from the recent 2008 oil spike.

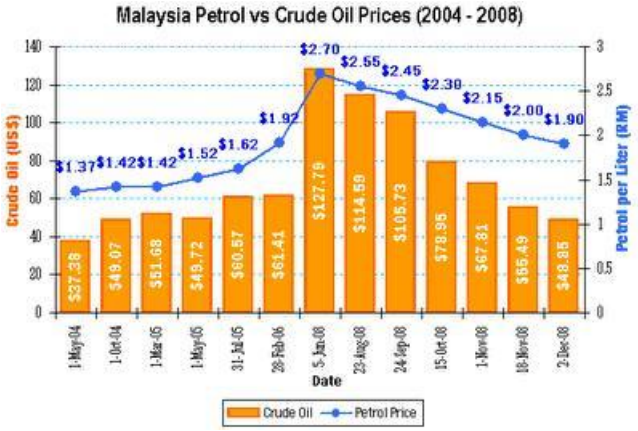

Figure 1.2: Malaysia petrol versus crude oil price

Biofuels are mostly originated from vegetable oils, waste oils and animal's fats. These are also consumed by human by either ways. With the increasing demands of these raw materials; it will eventually put a pressure onto the production of food. Therefore, it is best to be eased by developing a new and unexploited oil crops which isn't consumed as daily food but is capable of producing fats and oil for the industry.

Approximately there are 1 million rubber trees in 1,247,030 hectares of rubber trees estate in Malaysia. (RRIM, 08). A mature tree will produce rubber seeds. During the Japanese invasion in Malaya, rubber seeds are used as food. But nowadays rubber seeds have almost no other benefit towards economy growth except for the germination of new seedlings.

In term of environment consideration, Carbon dioxide (CO2) is the main greenhouse gas, and 70-75% of all CO2 emissions is due to combustion of fossil fuels.(Hoel,1996). The incensement in the concentration of carbon dioxide contributes to additional absorption of heat in the atmosphere.

1.3 Objective

- To synthesize biopetrol from fatty acids obtained from rubber seeds.
- To analyze the concentration production of biopetrol by heterogeneous catalytic cracking of fatty acid

1.4 Scope of Research

The scope has been identified for this study in order to achieve the objective. The scopes are:

- Extraction of fatty acid from rubber seeds.
- Catalytic cracking, a process of long chain fatty acid into smaller molecule.
- Determination of isooctane concentration using Gas Chromatography.

1.5 Rationale and Significance

The depletion in petroleum sources has led to an intensive search for alternative sources of energy and one of the best alternatives available is Biopetrol. Biopetrol can be continuously produced from renewable resources; therefore there will be no cut in energy for the usage of the whole world. Research on biodiesel has gained a lot of attention and has been developed and already been used on the road for diesel-used vehicles but not for biopetrol. With this research, the production of biopetrol can also be commercialized.

Biofuel has always been blamed for the increment in food price. In the United States of America, the price of corn grain increased twice the price due to the production of bioethanol. In 2008 global food controversy; Global Food Price, the increment in food price is caused 70% by weather and 30% caused by Biofuel. Using unexploited crops and non edible plant is indeed the best alternative. In Malaysia, there are more than 100 million hectares of rubber trees and its seeds are not being used either for daily consumption or any other usage.

Biopetrol is an environmentally friendly alternative liquid fuel. There has been renewed interest in the use of vegetable oils for making biopetrol due to its less polluting and renewable nature against the conventional petroleum diesel fuel. The biggest

difference between biofuels and petroleum feedstocks is the oxygen content. Biofuels have oxygen levels from 10% to 45% while petroleum has essentially none making the chemical properties of biofuels very different from petroleum. All have very low sulfur levels and many have low nitrogen levels.

CHAPTER 2

LITERATURE REVIEW

2.1 Petroleum or crude oil

The petroleum that we use today is from the remains of organic materials such as plants and animals that has been buried and gone trough enormous pressure, and heat as the layers increased. The mixtures are changed, breaking down into compounds made of hydrogen and carbon atoms. It takes millions of years for this formation to occur and can only take place within certain geological conditions. Under all these condition, only 2% of the organic mixture will eventually change into oil. We can not make our own oil reserve due to its lengthy amount of time which causes the oil to be considered as non renewable energy (rock talk)

The crude oil pumped out of the ground in a black thick liquid solution is also known as petroleum. Petroleum is a complex mixture of over 500 hydrocarbons that may have between 5 to 12 carbons per molecule. It is a petroleum-derived liquid mixture consisting mostly of aliphatic hydrocarbons and also some natural gas dissolved in it.

The alkanes from pentane (C5H12) to octane (C8H18) are refined into petrol. The ones from nonane (C9H20) to hexadecane (C16H34) are refined into diesel fuel and kerosene (primary component of many types of jet fuel), and the ones from hexadecane upwards into fuel oil and lubricating oil. At the heavier end of the range, paraffin wax is an alkane with approximately 25 carbon atoms, while asphalt has 35 and above. These akanes are usually cracked by modern refineries into more valuable products.

2.2 Biopetrol or biogasoline

In Commonwealth countries biogasoline is known as biopetrol. Generally, biopetrol is defined as fuel which has the same characteristic with petrol but is synthesized from renewable energy sources (Rahman et.al.2009) such as recent dead biological mass, wood scrap, used cooking oil and other waste. Meanwhile the fossil fuel is derived from long term dead biological material or predominantly called as biomass. Like traditionally produced gasoline, it contains between 6 (hexane) and 12 (dodecane) carbon atoms per molecule and can be used in internal-combustion engines.

2.3 Rubber Seed

Rubber Trees (*hevea brasiliensis*) are one of Malaysia's major agriculture plants where 12% of world rubber latex is produced. Matured Rubber trees produce seeds around once a year but currently the seeds give no economical benefits. The rubber plant which is widely used as a natural source of rubber has been reported to have oil rich seeds (Njoku et al., 1996). Presently, rubber seed oil does not find any major applications and hence even the natural production of seed itself remains under-utilized (Ramadhas, 2004). Although there are variations between compositions of rubber seed oil between different countries, a current research has found out the average composition of a rubber seed is 45.63% oil, 2.71% ash, 3.71% moisture, 22.17% protein, and 24.21%

carbohydrate, (Njoku et al., 1999). The high content of oil makes it suitable for oil production.

Table 2.1: Properties of rubber seed oil in comparison with other oils (Ramadhas et al, 2004)

Properties of rubber seed oil in comparison with the other oils

Property	Rubber seed oil	Sunflower oil	Rapeseed oil	Cotton seed oil	Soybean oil
Fatty acid composition (%)					
(i) Palmitic acid $C_{16:0}$	10.2	6.8	3.49	11.67	11.75
(ii) Stearic acid $C_{18:0}$	8.7	3.26	0.85	0.89	3.15
(iii) Oleic acid $C_{18:1}$	24.6	16.93	64.4	13.27	23.26
(iv) Linoleic acid $C_{18:2}$	39.6	73.73	22.3	57.51	55.53
(v) Linolenic acid $C_{18:3}$	16.3	0	8.23	0	6.31
Specific gravity	0.91	0.918	0.914	0.912	0.92
Viscosity (mm^2/s) at 40 °C	66.2	58	39. 5	50	65
Flash point (°C)	198	220	280	210	230
Calorific value (MJ/kg)	37.5	39.5	37.6	39.6	39.6
Acid value	34	0.15	1.14	0.11	0.2

2.4 Catalytic Cracking

Catalytic cracking is one of the routes for obtaining short chain where large hydrocarbon molecules are broken down into smaller and more highly branched paraffins and olefins of high octane numbers are produced with the presence of catalyst and high temperature. The basic to this mechanism is the availability of strongly acidic protons at high temperature on or in a supported matrix, which can initiate the carbonium ion reaction. (Hettinger, 1990) .This cracking also rearranges the molecular structure of hydrocarbon compound to convert simpler compound.

2.4.1 Mechanism of Cracking

Formation of carbonium ions which are required to initiate the propagation or steady-state reaction can be postulated to occur by either proton addition to an olefin by a Bronsted acid on the catalyst surface, or hydride extraction by a Lewis acid. Once carbonium ion species are formed on the catalyst surface, either through the addition of a

proton to an olefin or by Lewis acid extraction of a hydride ion, a chain reaction is initiated which involves extraction of a hydride ion by the adsorbed carbonium ion, causing adsorption of this molecule and replacement by the subsequent formed carbonium species. Migration of methyl groups along the chemically adsorbed skeletal hydrocarbon structure is facilitated. Hence, tertiary carbonium ion species are formed by methyl migration, thereby producing branched hydrocarbon species or higher octane number. The tendency for beta bond (the second carbon to carbon bond beyond the carbonium ion) rupture also is enhanced.

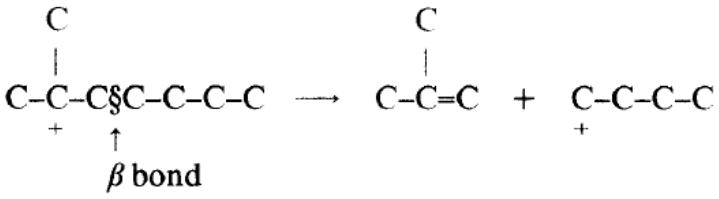

Figure 2.1: Mechanism Of Cracking

Cracking at the bond beta to a carbonium ion of a large, long, or linear hydrocarbon molecule, for example; the carbonium ion drawing a pair of electrons from the beta bond, results the formation of two smaller lower boiling molecules, namely an olefin at the carbonium ion site, and the remainder consisting of a primary hydrocarbon carbonium ion fragment. This fragment then either rearranges to a secondary or tertiary carbonium ion or goes through a chain transfer reaction as previously described, extracting a hydride ion from an incoming paraffin, and desorbing as a saturated hydrocarbon. (Hansford 1983, Voge 1983)

2.5 Fuller's Earth as a Catalyst

Although clay has been a most important mineral for man for centuries, the first recorded application of clay as a catalyst, was reported by Bondt, Deiman van

Troostwyk, and Lowrenberg who investigated the dehydration of alcohol in 1797 (Bondt et al., 1797).

Fuller's Earth, also known as calcium based bentonite, (Robertson,1986) is a type of clay that composes the minerals palygorskite and some smectite clays particularly calcium montmorillonite (Murray, 2000) or a mixture of the two and some of the other minerals that may be present in fuller's earth deposits which are; calcite, dolomite, and quartz. The Fuller's Earth is often a fine-grained material, high in water-content, with a high surface area and exhibiting high plasticity. (Smith et.al, 1996)

The term fuller's earth is used to describe clays which have sorptive and bleaching qualities (Murray, 2000). It is composed mainly of alumina, silica, iron oxides, lime, magnesia, and water in extremely variable proportions. It is semi-plastic or non-plastic and may or may not disintegrate easily in water. For centuries, Fuller's earth is used widely in petroleum process especially in bleaching and clarifying petroleum. It was this close association of clay, with its high capacity for adsorption of unwanted color bodies, for use in the petroleum industry as a decolorizer that lead to its eventual discovery as a superior catalyst for catalytic cracking in 1927 (Houdry, 1956; Oblad, 1983).

2.6 Oleic acid

Oleic acid is a mono-unsaturated omega-9 fatty acid found in various animal and vegetable sources. It has the formula $CH_3 (CH_2)_7CH = CH (CH_2)_7COOH$. It exists in all kinds of vegetable oil (Knothe et al, 1998). An average rubber seed oil from a rubber seed consist of 24.6% of oleic acid (Ramadhas et al, 2004).

Table 2.2: Properties of Oleic Acid

Properties	
Molecular formula	C18H34O2
Molar mass	282.4614 g/mol
Density	0.895 g/mL
Melting point	13-14 °C (286 K)
Boiling point	360 °C (633 K) (760mm Hg)
Solubility in water	Insoluble
Appearance	Pale yellow or brownish yellow oily liquid with lard-like odor

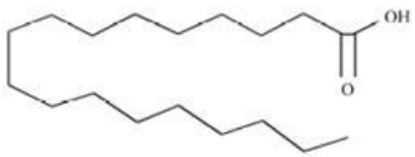

Figure 2.2: Oleic Acid Molecule Structure

2.7 Isooctane

2,2,4-Trimethylpentane, also known as isooctane or iso-octane, is an octane isomer which defines the 100 point on the octane rating scale (the zero point is n-heptane). It is an important component of petrol and is used as a reference fuel, in the development of new petrol (gasoline) blends. The fuel 'octane' number, familiar from the service station, is based on the 2,2,4-trimethylpentane standard. Isooctane can be produced by the cracking of oleic acid.

Table 2.2: Properties of Isooctane

Properties	
Molecular formula	C8H18
Molar mass	114.23 g mol−1
Density	688 kg/m3, liquid
Melting point	-107.38 °C, 166 K, -161 °F
Boiling point	99.3 °C, 372 K, 211 °F
Solubility in water	Immiscible
Appearance	colorless liquid

2.8 Gas Chromatography

Chromatography is used to separate a sample containing a mixture of compounds into isolated fractions. The gas chromatograph (GC) is a highly versatile tool for environmental analyses. Ideally, each compound is separated from the sample into a portion of the carrier gas stream, and then detected as it exits the column. To run a Gas Chromatography; analysts of interest needs to be separated from other parts of the sample in a reproducible way. Each time a standard or sample is run, the same retention times and signal strength at each peak should be obtained. Standards and unknowns run in different matrices and different levels should give a scalar response. That is, the peak area response at a given retention time should be directly proportional to concentration.

GC work requires a high level of analytical intuition, instrumental knowledge, time and practice preparing samples, and a fair amount of patience. Once a method has been developed to meet the two requirements previously stated, modern GC methods are considered to be a very efficient way of analyzing samples with many compounds. In gas chromatography (GC), a gaseous transport medium (mobile phase) carries the compound after it has been vaporized through a column which contains a (stationary phase). The stationary phase can either be a liquid (GLC = gas liquid chromatography) or a solid (GSC = gas solid chromatography). The mobile phase or carrier gas (N_2, He, P, or H_2) flows through the separation column and the single components are temporarily dissolved in the stationary phase (GLC) or adsorbed on the surface of the solid stationary phase.

This will depend on the chemical properties of the solute (sample components) and the solvents (stationary phase). It is this partitioning of the solute between the two phases that is responsible for the separation of the individual components or solutes. The intensity of the intermolecular interaction between the solute and the solvent governs the vapor pressure or the concentration of a particular solute within the mobile phase. This partition equilibrium of a solute between the two phases is described thermodynamically by the partition coefficient. In GLC with a gaseous mobile phase and a liquid stationary

phase this portion of the solute above the stationary phase can be described by Henry's law (providing the concentration of the solute within the stationary phase is fairly dilute). Liquid chromatography works on a similar principle, although a liquid sample is injected and a liquid stationary phase (on an inert, solid support) is used to separate the compounds (liquid-liquid chromatography). Liquid-solid chromatography (solid stationary phase) can also be used. The mass transport of the sample components takes place only in the mobile phase (carrier gas) and the residence time of a species or particular solute within a column of a given length will be short if this species spends most of its time in the mobile phase during the separation process. The quality of chromatographic separation (known as resolution) is high only if the components are found frequently in the stationary phase. For good separations of high resolution it is important that the different species undergo a selective interaction with the stationary phase. This interaction depends on the molecular structure and especially on the type of functional group and the stereochemistry (geometry) of the molecules of the solutes and the stationary phase.

The solvent (stationary phase) selectively retards the sample components according to their distribution coefficient. These component bands leave the column in the gas stream (solvent) and are recorded as a function of time by a detector and a computer data system (or stand-alone integrator). As previously mentioned, resolution of chromatographic peaks is related to two factors column efficiency and solvent efficiency. When the sample is injected with air, an air peak will come out at the time that it takes for the carrier gas to move through the column. This retention time is called the "dead time". The time that it takes for the compound to elute is the compound’s retention time, t_R. The capacity factor of the column for the compound of interest, K’, is found from the ratio of the adjusted retention time and the dead time.

CHAPTER 3

METHODOLOGY

3.1 Apparatus & Equipments

Below are the list of apparatus and equipments used during experiment in progress

a. Soxhlet extractor
b. Thermometer 110 °C
c. Round- bottom flask 250mL
d. Conical Flask 250mL
e. Filter & filter paper
f. 0.2µm syringe filter and Syringe 25ml
g. Rotary evaporator
h. Heating mantel 250ml
i. Anti-UV glass bottle
j. Gas chromatography Vials
k. Gas chromatography (agilent 6890N)